**SINTERING AND SYNTHESIS OF THE PSEUDOBROOKITE OXIDE (Fe_2TiO_5)
BY THE SOLID STATE REACTION**

KOITSU HIROTA* and RICHARD C. BRADT

*Department of Chemical and Metallurgical Engineering, Mackay School of Mines
University of Nevada, Reno, Reno, Nevada, 89557-0047, U.S.A.*

**Presently at the Department of Chemistry, Shonan Institute of Technology
1-25, Nishikaigan 1-Chome, Tsujido, Fujisawa-Shi, Kanagawa-Ken, 251, Japan*

Abstract- Pseudobrookite oxide Fe_2TiO_5 was synthesized by the solid state reaction. Synthetic pseudobrookite (Fe_2TiO_5) was prepared from high purity hematite (Fe_2O_3) and rutile (TiO_2) through conventional powder processing methods. This paper reports a synthetic way to yield a fine pseudobrookite powder suitable for specimen consolidation and sintering.

Key words- pseudobrookite (Fe_2TiO_5), hematite, rutile, X-ray diffraction, EPR

INTRODUCTION

Both iron oxide ceramics and titanium oxide ceramics are widely utilized for electronic devices. The properties of these polycrystalline ceramics are dependent upon the microstructure, so that it is important in a general sense to fundamentally understand the microstructural development of ceramics. Many modern industrial ceramics, especially commercial refractories were initially produced directly or indirectly from naturally occurring minerals. Examples include hematite (Fe_2O_3) and rutile (TiO_2). The most important iron mineral is hematite (Fe_2O_3). Iron (III) oxide occurs naturally as the mineral hematite, the principal ore of iron. Titanium is relatively abundant in igneous rocks in the earth crust. The most important titanium minerals are ilmenite ($\text{FeO} \cdot \text{TiO}_2$), titaniferous magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{FeO} \cdot \text{TiO}_2$), rutile (TiO_2) and sphene ($\text{CaO} \cdot \text{TiO}_2 \cdot \text{SiO}_2$). In the last decade there has been a considerable increase in the understanding of the basic phenomena occurring in sintering and a number of authors have been reported[1-11]. We have recently reported [11] investigations for the synthetic way of forsterite (Mg_2SiO_4) from high purity silica (SiO_2) and magnesia (MgO), and for their density and grain growth, as well as for the grain size/density relationship. We have studied grain growth and quite successfully expressed their results[9-13]. The sintering behavior of ceramics was studied mainly in model systems with simple compositions[14,15]. Although many papers dealing with sintering behavior have been published on this system, we think that the sintering behavior is not fully understood. These investigations suggested that it is important to understand microstructural development of ceramics. We have been studying the effect of additive content on the densification behavior and the microstructure development by sintering in the system Fe_2O_3 - TiO_2 . (unpublished data). This paper reports a synthetic procedure to yield a fine pseudobrookite powder suitable for specimen consolidation and sintering.

EXPERIMENTAL PROCEDURE

Starting materials are reagent special grade oxides ("Baker Analyzed"). After drying at 400 °C for 1 hour, the oxides were mixed in the proportion of 1 : 1 (molar basis) for several hours at room temperature using a high alumina mortar and pestle. The preheated mixtures at 400 °C for 1 hour of iron oxide and titanium oxide were fired in air at 1100 °C in a furnace at a rate of 7 °C/min. to 1100 °C and held for 1 hour using a high alumina crucible. These samples were then quenched gradually to room temperature in the desiccator cabinet in silica gels and analyzed by X-ray diffraction technique. The partially reacted powder after the initial firing were mixed for several hours at room temperature using the same high alumina mortar and pestle. The mixed partially reacted products after the initial firing were fired again under the same set of

conditions. The powders were mixed and fired five times successively under the same set of conditions. The X-ray diffraction technique was used for determination of the reaction of the powders. The X-ray powder diffraction analysis was made using a Siemens Analytical X-Ray Instruments. The X-ray spectra were stored and processed in a Nicolet dedicated computer (Nicolet Instrument Corp., Madison, WI). The X-band (at 9.265 GHz) electron paramagnetic resonance spectroscopy (EPR) experiments were performed at 77 K. EPR measurements were made using a JEOL RE-2X Operating Instruments (JES-FE and JES-RE) and sample temperature was maintained at 77 K using Glass Instruments liquid nitrogen cryostat. The samples were placed in quartz EPR tubes (2 mm inside diameter) that had been gassed with nitrogen. Spectra were recorded into a computer which was used to plot the figures and calculate g-values shown. g-values were calculated using an external standard of Mn^{2+} in MgO . X-band EPR-operating conditions were magnetic-field modulation, 100 KHz; microwave power, 1 mW; time constant, 1 sec; sweep time, 8 sec; field modulation amplitude, 0.16 mT (millitesla); temperature, 77 K; frequency, 9.265 GHz (X-band); field, 330 mT/G $\pm$ 10 mT/G. g-values and field scales used in the figures are approximate.

RESULTS AND DISCUSSION

Figure 1 illustrates the $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - TiO_2 phase diagram[16]. One of the most notable features of the phase equilibria diagrams in the system iron oxide $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - titanium oxide TiO_2 in air are that, hematite(ss) is the primary crystalline phase in the composition range 12-27 wt.% TiO_2 with liquidus temperatures decreasing from 1524 to 1493 °C, and a liquid of the latter TiO_2 content is in equilibrium with hematite(ss) as well as pseudobrookite(ss) at what appears as a eutectic situation at 1493 °C, as more TiO_2 is added to the mixtures, pseudobrookite is the primary crystalline phase, and liquidus temperatures increase.

Fig. 1.

The System $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ - TiO_2 in air
after J. B. MacChesney and Arnulf Muan,
Am. Mineral., **44**, 938 (1959).

The X-ray diffraction pattern was obtained and reviewed to determine the extent of the reaction of the powders as shown in Fig. 2. Prior to firing, the hematite-rutile mixture revealed (as shown in Fig.2(c)) those diffraction peaks characteristic of a hematite Fe_2O_3 (two theta = 33.0°, 49.5° and 55.3° :circles, shown in Fig.2(a)) and a rutile TiO_2 (two theta = 48.1° and 54.2° :triangles, shown in Fig.2(b)). After the initial one hour firing at 1100 °C, the diffraction pattern included the high intensity peak of a hematite Fe_2O_3 (two theta = 33.0°, shown in Fig.2(d)). After five successive firings under the same set of conditions completed the synthesis reaction to yield single phase pseudobrookite Fe_2TiO_5 as is evident from the X-ray diffraction pattern as shown in Fig.2(e). This pattern closely agrees with the JCPDS X-ray diffraction pattern for pseudobrookite[17].

X-band EPR (Electron Paramagnetic Resonance spectroscopy) spectra at low temperature were obtained as shown in Fig. 3. Hematite gives signal at $g = 1.997$ as shown in Fig.3(a). Rutile gives signal at $g = 1.988$ as shown in Fig.3(b). The scan at 77 K gave both signals of the mixture of oxides (see Fig.3(c)) but at 77 K the EPR signals of the synthetic pseudobrookite broadened and ceased to be detectable as shown in Fig.3(d). The EPR scan at 77 K served as a measure of the extent of the reaction of the mixtures.

The resulting pseudobrookite powder was then milled for several hours and passed through a 400 mesh (38 μm) screen to yield a fine pseudobrookite powder suitable for specimen consolidation and sintering. Utilizing that ceramic powder, specimens were pressed then sintered for several time/temperature conditions between 1400 °C and 1600 °C and

Fig. 2.

X-ray diffraction of

- (a) the hematite Fe_2O_3
- (b) the rutile TiO_2
- (c) the hematite-rutile mixture
- (d) after initial firing for 1 hr. at 1100 °C
- (e) after five successive firings for 1 hr. at 1100 °C (synthetic pseudobrookite Fe_2TiO_5)

Fig. 3.

X-band EPR spectra at low temperature of

- (a) the hematite Fe_2O_3
 - (b) the rutile TiO_2
 - (c) the hematite-rutile mixture
 - (d) after five successive firings 1 hr. at 1100 °C (synthetic pseudobrookite Fe_2TiO_5)
- EPR-operating conditions are described in EXPERIMENTAL PROCEDURE.

Fig. 4. Micrographs of (a) the hematite-rutile mixture
(b) Synthetic Pseudobrookite Fe_2TiO_5

systematically investigated for their density and grain growth, as well as for the grain size/density relationship. To facilitate the application of naturally occurring minerals such as pseudobrookite for industrial applications, there is a complementary course of study and research that is equally valuable to gain a fundamental understanding of the mineral. That approach is to prepare and investigate the refractory compound in a form produced from synthetic components[10]. It has been shown by a number of authors that the basic phenomena in the grain-boundary migration[4], and grain growth mechanism for monodispersed ZrO_2 [2,7]. They reported that at the sintering temperature a considerable grain growth generally takes place, resulting in a drastic decrease in the total available grain - boundary area. As the microstructure of the compacts will be largely affected by this grain boundary migration.

We showed a microstructure of the synthetic pseudobrookite (Fig.4).

ACKNOWLEDGEMENTS

One of us (K. Hirota) wishes to acknowledge the Private University Promotion Foundation of Japan for funds to enable his visit to America to undertake the work described. He would also like to thank to the Shonan Institute of Technology for grants.

We wish to thank the Nevada Mining and Mineral Resources Research Institute (Bureau of Mines, Department of Interior; Grant No. G 1154132) for financial support in the form of an MMRI Fellowship (Y.H.H.).

REFERENCES

1. H. V. Atkinson, *Acta. Metall.*, 36[3] 469-91 (1988)
2. T. Ogihara, N. Mizutani, and M. Kato, *J. Am. Ceram. Soc.*, 72[3] 421-26 (1989)
3. D.F.K. Hennings, R. Janssen, and P.J.L. Reynen, *J. Am. Ceram. Soc.*, 70[1] 23-27 (1987)
4. Yet-Ming Chiang and W. D. Kingery, *J. Am. Ceram. Soc.*, 72[2] 271-77 (1989)
5. E. A. Barringer and H. K. Bowen, *Comm. Am. Ceram. Soc.*, C-199 - C-201 (1982)
6. M. Drofenik, *J. Am. Ceram. Soc.*, 70[5] 311-14 (1987)
7. F. F. Lange and M. M. Hirlinger, *J. Am. Ceram. Soc.*, 70[11] 827-30 (1987)
8. G. Zhilun, G. Suhua and Z. Xiaowen, *J. Am. Ceram. Soc.*, 72[3] 486-91 (1989)
9. T. Senda and R. C. Bradt, *J. Am. Ceram. Soc.*, 73[1] 106-14 (1990)
10. J. B. Baldo and R. C. Bradt, *J. Am. Ceram. Soc.*, 71[9] 720-25 (1988)
11. Y. H. Han, K. Hirota and R. C. Bradt, *Proc. Int. Cong. Sintering*, in press (1991).
12. J. A. Kuszyk and R. C. Bradt, *J. Am. Ceram. Soc.*, 56[8] 420-423 (1973)
13. J. J. Cleveland and R. C. Bradt, *J. Am. Ceram. Soc.*, 61 478-81 (1978)
14. J. Wong and W. G. Morris, *Am. Ceram. Soc. Bull.*, 53[11] 816-20 (1974)
15. J. Wong, *J. Appl. Phys.*, 51[8] 4453-59 (1980)
16. J. B. MacChesney and Arnulf Muan, *Am. Mineral.*, 44, 938 (1959)
17. Selected Powder Diffraction Data for Minerals, (9-182), (21-1276), and (32-469)
Published by the JCPDS, Pennsylvania, U.S.A. (1974)